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# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Improvements in or relating to the Polymerisation of Olefines

We, PETROCHEMICALS LIMITED, a British Company, of 170, Piccadilly, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the polymerisation of olefines by the so-called Ziegler low-pressure process, which involves polymerisation of an olefine in the presence of a Ziegler catalyst under a pressure which is below 500 atmospheres and usually below 50 atmospheres e.g. up to about 5 to 10 atmospheres.

The term Ziegler catalyst as used herein means a Ziegler catalyst formed by mixing (or otherwise bringing together) at least two Ziegler catalyst-forming components and for the purposes of the present invention such catalyst-forming components are defined as consisting of at least one "A" component and at least one "B" component, an A component being a compound of a metal of Group IVA, VA, VEA or VIII of the Periodic Classification and particularly of Group IVA, VA or VIA thereof and more particularly of Group IVA e.g., titanium; and a B component being a reducing agent selected from the Group I, II or III metals tin or lead, and also alloys of such metals; the organo-metallic compounds (or complexes thereof) of Group I, II or III metals, tin or lead; the hydrides (or complexes thereof) of Group I, II or III metals; and the organo-boron compounds or addition complexes thereof, and particularly the organo-metallic compounds of Group III metals, e.g., aluminium. The term "organo-metallic compound" means a compound (other than an inorganic metal carbide) in which the metal is directly attached to a carbon atom. Polymerisation by the Ziegler low-pressure process is described in for example U.K.

Patent Specifications Nos. 799,392; 799,823; 801,031; 819,867; 820,263 and 820,264, polymerisation being effected conveniently, though not necessarily, in the presence of an inert non-aqueous liquid (e.g., a hydrocarbon) which is often referred to in the Ziegler art simply as an inert solvent. The present invention is particularly, but in no way exclusively, suited to the polymerisation of ethylene in the presence of a Ziegler catalyst formed by mixing an aluminium trialkyl or an aluminium alkyl halide, in particular an aluminium dialkyl monohalide, with a titanium salt, e.g. titanium tetrachloride. The polymerisation of ethylene in the presence of such a catalyst is described in Specification No. 803,557.

Examples of Ziegler catalysts which can be used in the Ziegler low pressure process with which the present invention is concerned are those formed by mixing at least one compound, preferably a halide for example a tetrachloride or trichloride, of a metal of Groups IVA, VA or VIA and in particular Group IVA of the Periodic Table, e.g., titanium tetrachloride and/or trichloride with at least one of the following compounds:—

- (a) an aluminium trialkyl—
- (b) an aluminium compound of the general formula  $R_1R_2AlX$ , wherein  $R_1$  and  $R_2$  are similar or dissimilar and each represents hydrogen or a hydrocarbon radical and  $X$  represents hydrogen, halogen, an alkyloxy or aryloxy group or the residue of a secondary amine or an N-substituted amide, mercaptan, thiophenol; carboxylic acid or sulphonic acid—
- (c) magnesium and zinc alkyls and Grignard compounds.

If a compound of the general formula  $R_1R_2AlHal$  is used, the metals of Groups IVA

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to VIA of the Periodic Table may be replaced by a metal belonging to Group VIII of the Periodic Table, such as nickel, cobalt, or platinum; or by manganese.

5 According to the present invention a Ziegler low-pressure process for preparing a polyolefine, particularly but not exclusively a polyethylene, is provided in which an olefine is polymerised with the aid of a Ziegler catalyst (as herein defined), wherein a minor proportion relative to the olefine polymerised of a boron halide is added to the polymerisation zone or to a component (such as the olefine to be polymerised, of the solvent (when used) or the formed Ziegler catalyst) supplied to the polymerisation zone.

10 It has been found that by carrying out a Ziegler low-pressure olefine polymerisation process in the presence of a minor proportion of a boron halide relative to the olefine (which is preferably ethylene) effective and flexible control of the molecular weight of the resulting polymer product may be obtained. Thus in accordance with the present invention a Ziegler low-pressure olefine polymerisation process may be carried out in the presence of a minor proportion of one or more of the following compounds: boron trifluoride, boron trichloride, boron tribromide and boron triiodide, of which boron trifluoride is at present preferred.

20 An olefine is advantageously polymerised in accordance with the present invention by forming a Ziegler catalyst by mixing either aluminium tri-isobutyl or aluminium di-ethyl monochloride with titanium tetrachloride in the presence of an essentially non-aromatic solvent, forming a catalyst-containing reaction medium by diluting the resulting catalyst mixture with further solvent and effecting polymerisation by passing an olefine containing a minor proportion of boron trifluoride through the reaction medium maintained at for example 40° C. The amount of boron halide additive such as boron trifluoride required is, in general, relatively small, for example of the order of 1% or below by weight of the olefine polymerised. Thus the amount of boron halide employed is conveniently between 0.001 and 10 molar per cent of the olefine polymerised; preferably it is between 0.002 and 1 molar per cent of the olefine polymerised. It will be understood that the amount of boron halide required in a particular low-pressure Ziegler polymerisation process will usually be dependent to some extent on the nature of the catalyst-forming components employed in forming the Ziegler catalyst used; and also the relative molar proportions in which the catalyst-forming components are mixed, as well as on the polymerisation conditions in general. Hence when applying the process of the present invention to a given olefine polymerisation process, an initial trial may often be necessary

to ascertain the optimum amount of halide e.g., boron trifluoride to be used. The amount of polymer formed in the particular low-pressure process *per se* i.e., without using the boron halide additive of the present invention, may be taken as a basis and then polymerisation is carried out with say 0.002 molar per cent of e.g. boron trifluoride based on the molar quantity of olefine equivalent to the amount of polymer formed. In this connection it should be noted that the presence of the boron trifluoride may alter the yield of polymer somewhat, and this factor may therefore have to be taken into account when calculating the amount of boron trifluoride to be used in the subsequent run.

Polymerisation is conveniently carried out using a reaction medium comprising the catalyst dissolved and/or suspended in a liquid saturated hydrocarbon e.g. iso-octane or a light petroleum distillate boiling at about 100° C., the catalyst being obtained by mixing aluminium diethyl monochloride and titanium tetrachloride as the catalyst-forming components, each component being present to the extent of 2 to 20 millimoles and preferably about 5 millimoles per litre (i.e. a molar ratio of Al:Ti of about 1:1), and the amount of boron trifluoride is preferably between 0.05 and 2.0 moles per mole of titanium in the catalyst.

Boron trifluoride may be supplied to the polymerisation reaction medium either by direct addition to the olefine feed or as a separate feed, preferably in admixture with a liquid diluent such for example as the solvent present during polymerisation in view of the small quantities of boron halide additive required.

The present invention is applicable to both batch and continuous operation and it will be appreciated that continuous operation offers more than one feed stream to which the boron halide may be added continuously at either a constant or a varying rate; alternatively it can be added intermittently during the course of olefine polymerisation. In batch operation the boron halide may be added to the catalyst mixture or to the solvent before polymerisation is commenced.

The Ziegler catalyst employed in olefine polymerisation in accordance with the present invention can be prepared in the presence of the boron halide additive, and according to a further feature of the present invention, a Ziegler catalyst is formed by mixing an aluminium trialkyl or an aluminium alkyl halide with a titanium salt (preferably a titanium halide, e.g. a tetrahalide) in the presence of a boron halide, the amount of said boron halide not exceeding about 5 moles per mole of titanium. Preferably the organo-aluminium compound is an aluminium dialkyl monochloride and the titanium salt is titanium tetrachloride.

The technique employed for polymerising olefines by the low-pressure process using a Ziegler catalyst has already been described. Thus in polymerising ethylene by the Ziegler process the ethylene at low-pressure, e.g. up to about 4—5 atmospheres, is conveniently passed into a dispersion of the catalyst in an inert liquid hydrocarbon medium which is maintained at an elevated temperature conveniently between about 30 and 50° C., e.g. about 35—40° C., the polymerisation being carried out in a jacketed vessel fitted with a stirrer. Polymerisation can be carried out batchwise by adding the required amount of catalyst to the hydrocarbon medium and then bubbling in ethylene until the reaction slurry which is formed during polymerisation becomes too thick to stir, or continuously by providing means for adding fresh catalyst continuously or intermittently to the reactor and a draw-off line at the bottom of the reactor through which reaction slurry can be removed periodically for working-up to isolate and purify the resulting polyethylene. In continuous operation fresh hydrocarbon medium is supplied to the reactor during polymerisation in order to maintain a substantially constant slurry concentration therein. The catalyst concentration in the reaction mixture can be varied within relatively wide limits, though it will be appreciated that for economic reasons it is advantageous to employ the minimum concentration required to produce a desired yield and rate of polymerisation. It is convenient to express the catalyst concentration in terms of the concentration of titanium tetrahalide in millimoles per litre of reaction medium and in such cases it is usually sufficient to use a catalyst concentration of between about 5 and 30, and preferably between about 5 and 15 millimoles of the titanium tetrahalide per litre.

Polymerisation can be effected with ease at moderately elevated temperatures, for example about 40° C., and at ordinary or somewhat elevated pressures of the order of several atmospheres or even higher.

The immediate polymerisation product is frequently a brown-coloured slurry comprising a suspension of the polyethylene in the solvent which also contains the catalyst, and this slurry is then treated with a reagent such as methanolic hydrochloric acid to decompose the catalyst to give soluble products which can be removed by separating the methanolic phase and washing the resulting white polymer product with aqueous solutions containing small amounts, e.g., 1% by weight, of acid and alkali respectively. Finally the polymer product is dried and processed as desired, e.g., by extrusion into ribs, for marketing.

Although for the purposes of the present invention it is possible to use as the olefine feed a technical grade olefine obtained from industrial sources, e.g., refinery operations,

and containing the usual impurities, it is generally preferred to achieve high purity in the olefine feed, the catalyst-forming components and the solvent for the polymerisation medium which may be a liquid hydrocarbon or certain halogenated hydrocarbons. Thus although small quantities of other olefines which will polymerise or copolymerise with ethylene can often be tolerated, it is desirable to use an olefine (or olefine mixture) which is as free as is practicable from all other unsaturated hydrocarbons and also any non-hydrocarbon organic compounds; and the same considerations apply broadly to the solvent. In the olefine feed the quantity of all impurities (disregarding hydrogen and saturated hydrocarbons), should preferably be reduced to less than 30 parts per million by weight (e.g., acetylene 1 part per million, oxygen 15 parts per million and carbon monoxide 5 parts per million).

The purification of the olefine feed and the solvent employed in the process may be carried out in any way convenient, e.g., by treatment with catalyst-forming components as described in the Specification of British Patent Application No. 33,097/55 (Serial No. 815,310) or in the case of the solvent by treatment with concentrated sulphuric acid followed by water-washing and distilling over calcium hydride or sodium under nitrogen. Treatment of the olefine with ammoniacal cuprous chloride or catalytic hydrogenation with a platinum catalyst may be employed to eliminate acetylene from the olefine feed.

In certain cases an impurity in the form of a compound or compounds selected from a group comprising Lewis bases (the term "Lewis base" is defined in the specification of our copending British Patent Application No. 23,906/56 (Serial No. 815,113)) and compounds having an active hydrogen atom in the molecule, i.e., a hydrogen atom which can be substituted as a result of reaction between the compound and a metal or metal salt (as described in the specification of our copending British Patent Application No. 23,907/56 (Serial No. 815,112)) may be present as impurity in the olefine to be polymerised or in some other constituent of the reaction mixture, e.g., the organic solvent used in the Ziegler polymerisation. Such impurities usually have a modifying effect on the molecular weight of the resulting polyolefine and consequently in some cases it will be desirable to remove substantially all Lewis bases and/or hydrogen-active compounds from the olefine or other component(s) of the reaction medium prior to adding the boron halide to the reaction mixture.

According to a further feature of the present invention a Ziegler low-pressure process for preparing a polyolefine is carried out under conditions in which the maximum permissible concentration in the reaction mixture of a

Lewis base (or bases) or a compound (or compounds) having an active hydrogen atom in the molecule and which is/are present as impurity in the olefine or other component supplied to the polymerisation zone is below about 0.001 molar per cent of the amount of olefine polymerised.

Since a gaseous olefine is generally polymerised by passing the gas through a polymerisation zone containing a liquid phase reaction mixture under conditions in which only a proportion of the gas may take part in the polymerisation reaction, it will be appreciated that only a proportion of the boron halide additive such as boron trifluoride which has been added to the gaseous olefine feed may be effective as a molecular weight modifier and consequently it is advisable when employing such a technique to determine experimentally the amount of gaseous boron halide additive to be employed in order to achieve a particular effect in the polymerization.

The present invention is illustrated by the following example:—

#### EXAMPLE.

A polymerisation reactor provided with a stirrer, a dip tube for admission of ethylene and means for heating or cooling the reactor was used. A suspension of a Ziegler catalyst in iso-octane was prepared in the reactor by adding an iso-octane solution of diethyl aluminium monochloride to an iso-octane solution of titanium tetrachloride and mixing the components at 20° C. under an atmosphere of ethylene. The quantities of the catalyst-forming components were such as to give a catalyst having an Al/Ti ratio as represented by an Al/Ti concentration of 6.5/5.0 millimoles per litre of iso-octane. The catalyst suspension was then rapidly heated to the polymerisation temperature of 40° C. and ethylene containing traces of acetylene and 1% of boron trifluoride was passed through it for 2 hours. The resulting polymeric product was then worked-up by treatment with acidic methanol, washing and drying to give a polymer of intrinsic viscosity 2.1 as compared with a polymer of intrinsic viscosity 2.6 obtained under otherwise identical conditions but in the absence of the boron trifluoride.

#### WHAT WE CLAIM IS:—

1. A Ziegler low-pressure process for preparing a polyolefine in which an olefine is polymerised with the aid of a Ziegler catalyst (as herein defined), wherein a minor proportion relative to the olefine polymerised of a boron halide is added to the polymerisation zone or to a component supplied to the polymerisation zone.

2. A process as claimed in Claim 1, wherein the amount of said boron halide is not more than about 1% by weight of the olefine polymerised.

3. A process as claimed in Claim 1 or

Claim 2, wherein the olefine is ethylene.

4. A process as claimed in any one of the preceding claims, wherein said boron halide is boron trifluoride.

5. A process as claimed in Claim 4, wherein the amount of boron trifluoride employed is between 0.002 and 1 molar per cent of the olefine polymerised.

6. A process as claimed in any one of the preceding claims, wherein the Ziegler catalyst used is one formed by mixing an aluminium trialkyl or an aluminium alkyl halide with a titanium trihalide or tetrahalide.

7. A process as claimed in any one of the preceding claims, wherein the Ziegler catalyst is one formed by mixing aluminium diethyl monochloride with titanium tetrachloride.

8. A process as claimed in any one of the preceding claims, wherein polymerisation is carried out under conditions in which the maximum permissible concentration in the reaction mixture of a Lewis base (or bases) or a compound (or compounds) having an active hydrogen atom in the molecule and which is/are present as impurity in the olefine or other component supplied to the polymerisation zone is below about 0.001 molar per cent of the amount of olefine polymerised.

9. A process for preparing a polyethylene substantially as hereinbefore described with special reference to the example.

10. A polyolefine when prepared by the process claimed in any one of the preceding claims.

11. A Ziegler catalyst formed by mixing an aluminium trialkyl or an aluminium alkyl halide with a titanium salt in the presence of a boron halide in an amount not exceeding about 5 moles of titanium.

12. A Ziegler catalyst as claimed in Claim 11, wherein the titanium salt is a titanium halide.

13. A Ziegler catalyst as claimed in Claim 12, wherein said halide is a tetrahalide.

14. A Ziegler catalyst as claimed in Claim 12 or Claim 13, wherein said halide is a chloride.

15. A Ziegler catalyst as claimed in Claim 14, wherein the organo-aluminium compound is an aluminium dialkyl monochloride and the titanium salt is titanium tetrachloride.

16. A process for preparing a polyolefine, which comprises polymerising an olefine by the Ziegler low-pressure process using a catalyst as claimed in any one of Claims 11 to 15.

17. A process as claimed in Claim 16, wherein the olefine is ethylene.

18. A polyethylene when prepared by the process claimed in Claim 17.

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## PROVISIONAL SPECIFICATION

## Improvements in or relating to the Polymerisation of Olefines

We, PETROCHEMICALS LIMITED, a British Company, of 170, Piccadilly, London, W.1, do hereby declare this invention to be described in the following statement:—

5 The present invention relates to the polymerisation of olefines by a so-called low pressure polymerisation process, i.e. a process involving polymerisation of the olefin, for example ethylene, propylene or butylene, or a mixture containing two or more such olefins, in the presence of a catalyst and under a pressure of below 500 atmospheres, the term "low-pressure" being used in order to distinguish the process broadly from known processes of olefin polymerisation under pressures of the order of 1000 atmospheres or more. Examples of catalysts which can be used in such low pressure polymerisation processes include catalysts formed by mixing two or more catalyst-forming components, said components comprising at least one compound of a metal of Groups IV to VI of the Periodic Table and at least one of the following compounds:—

- 25 (a) an aluminium trialkyl
- (b) an aluminium compound of the general formula  $R_1R_2AlX$ , wherein  $R_1$  and  $R_2$  are similar or dissimilar and each represents a hydrogen atom or a hydrocarbon radical and X represents a hydrogen atom, a halogen atom, an alkyloxy group or an aryloxy group or the residue of a secondary amine or amide, mercaptan, thiophenol, carboxylic acid or sulphonic acid
- 30 (c) magnesium and the zinc alkyls and Grignard compounds.

If a compound of the general formula  $R_1R_2AlHal$  is used, the metals of Groups IV to VI of the Periodic Table may be replaced by a metal belonging to Group VIII of the Periodic Table, such as nickel, cobalt, platinum, or by manganese.

The present invention relates particularly but not exclusively to the polymerisation of ethylene by the low-pressure method (hereinafter referred to as "Ziegler polymerisation") as described, for example, in the specification of British Patent Application No. 2083/55 (Serial No. 803,557) whereby ethylene is polymerised in the presence of a Ziegler catalyst formed by a mixture of catalyst-forming components comprising a titanium salt and an aluminium tri-alkyl or an aluminium di-alkyl monohalide.

55 According to the present invention an olefine, preferably a highly purified olefine, is polymerised by a low-pressure polymerisation process in the presence of a minor proportion of a halide of an element of Group IIIB of the Periodic Classification.

The important elements of Group IIIB of

the Periodic classification, at least in so far as the present invention is concerned, are boron and aluminium, and it has been found that by carrying out a low-pressure polymerisation of an olefine and particularly ethylene in the presence of a minor proportion of a boron or aluminium halide an effective and flexible control of the molecular weight of the polymer product may be obtained. Thus in accordance with the present invention a low-pressure olefine polymerisation process may be carried out in the presence of a minor proportion of one or more of the following compounds: boron trifluoride, boron trichloride, boron tribromide, boron triiodide, aluminium fluoride, aluminium chloride, aluminium bromide or aluminium iodide. Of these halides boron trifluoride and aluminium chloride are at present preferred.

An olefine is advantageously polymerised in accordance with the present invention using a catalyst formed by mixing either aluminium tri-isobutyl or aluminium di-ethyl monochloride with titanium tetrachloride, polymerisation being carried out in the presence of a minor proportion of boron trifluoride or aluminium chloride, and if desired, boron trifluoride and aluminium chloride may be present together in the reaction mixture.

The amount of halide additive such as boron trifluoride or aluminium chloride required is, in general, relatively small, for example of the order of 1% or below by weight of the olefine feed. Thus the amount of boron or aluminium halide employed is conveniently between 0.001 and 10 molar per cent of the olefine which is polymerised; preferably it is between 0.002 and 1 molar per cent of the olefine which is polymerised. It will be understood that the amount of boron or aluminium halide required is a particular low-pressure polymerisation process will usually be dependent to some extent on the nature of the catalyst-forming components employed and their relative molar proportions, as well as on the reaction conditions in general. Hence when applying the process of the present invention to a given olefine polymerisation process, an initial trial may often be necessary to ascertain the optimum amount of halide e.g. boron trifluoride or aluminium chloride to be used. The amount of polymer formed in the particular low-pressure process *per se*, i.e. without using the process of the present invention, may be taken as a basis and then polymerisation is carried out with say 0.002 molar per cent of boron trifluoride or aluminium chloride based on the molar quantity of olefine equivalent to the amount of polymer formed. In this connection it should be noted that presence of the fluoride or chloride may

alter the yield of polymer somewhat, and this factor may therefore have to be taken into account when calculating the amount of fluoride or chloride to be used in the subsequent run.

When polymerisation is carried out in the liquid phase, i.e. with the catalyst dissolved and/or suspended in solvent such as a saturated hydrocarbon e.g. iso-octane, using aluminium diethyl monochloride and titanium tetrachloride as the catalyst-forming components, each compound being present to the extent of 2 to 20 millimols and preferably about 5 millimols per litre (i.e. a molar ratio of Al:Ti and about 1:1) the amount of boron trifluoride or aluminium chloride is preferably between 0.05 and 2.0 millimols per mol of aluminium or titanium in the catalyst.

Normally gaseous halides such as boron trifluoride may be supplied to the polymerisation reaction medium either by addition to the olefine feed or, as with the other halides, as a separate feed, preferably in admixture with a liquid diluent, such for example as the solvent present during polymerisation, in view of the small quantities required.

The present invention is applicable to both batch and continuous operation and it is clear that continuous operations offers more than one feed stream to which the halide may be added continuously at either a constant or a varying rate: alternatively it can be added intermittently during the course of olefine polymerisation. In batch operation the halide may be added to the catalyst mixture or to one of the optional components of the reaction mixture, e.g. to the solvent, before polymerisation starts.

Although for the purposes of the present invention it is possible to use as the olefine feed a technical grade olefine containing the usual impurities, it is generally preferred to use a very pure olefine and also very pure catalyst-forming components as well as very pure optional components of the polymerisation reaction mixture such as a solvent which may be a liquid hydrocarbon or certain halogenated hydrocarbons. Thus it is desirable to use an olefine (or olefine mixture) which is as free as is practicable from all other unsaturated hydrocarbons and also any non-hydrocarbon organic compounds; the same considerations apply broadly to the optional components of the reaction mixture such as the organic solvents. In the olefine feed the quantity of all impurities (disregarding hydrogen and saturated hydrocarbons), should preferably be reduced to less than 30 ppm. by weight (e.g. acetylene 1 ppm., oxygen 15 ppm and carbon monoxide 5 ppm).

The purification of the olefine feed and the solvent employed in the process may be carried out in any way convenient, e.g. by treatment with catalyst-forming components as described in the Specification of British

Patent Application No. 33097/55 (Serial No. 815,316), or by treatment with sulphuric acid (using dilute acid to treat the olefine and more concentrated acid to treat the solvent) and then distilling over calcium hydride.

Treatment of the olefine with ammoniacal cuprous chloride or catalytic hydrogenation may be employed to eliminate acetylene from the olefine feed.

In certain cases an impurity in the form of a compound or compounds selected from a group comprising Lewis bases (a Lewis base is a compound having in the molecule an electron pair available for sharing) and compounds having an active hydrogen atom in the molecule, i.e. a hydrogen atom which can be substituted as a result of reaction between the compound and a metal or metal salt, may be present as impurity in the olefine to be polymerised or in some other constituent of the reaction mixture, e.g. the organic solvent used in the Ziegler polymerisation. Such impurities usually have a modifying effect on the molecular weight of the resulting polyolefine and consequently in some such cases it will be desirable to remove substantially all Lewis bases and/or hydrogen-active compounds from the olefine or other component(s) of the reaction medium prior to adding the boron or aluminium halide to the reaction mixture.

According to a further feature of the present invention an olefine is polymerised by a low-pressure polymerisation process under reaction conditions in which the maximum permissible amount of a Lewis base (or bases) or a compound (or compounds) having a hydrogen active atom in the molecule and present as impurity in the olefine or some other component of the reaction mixture, is below about 0.001 molar per cent of the amount of olefine polymerised under the reaction conditions.

Since the olefine to be polymerised is generally passed as a gas through the liquid phase reaction mixture and under conditions in which only a proportion of this gas may take part in the polymerisation reaction, it will be appreciated that only a proportion of boron trifluoride in a gaseous olefine may be effective in acting as a molecular weight modifier.

The present invention is illustrated by the following examples in which the parts are by weight unless otherwise stated and the relationship between the parts by weight and the parts by volume is that which subsists between the kilogram and the litre.

#### EXAMPLE I.

A suspension of a Ziegler catalyst in iso-octane was prepared as follows. Titanium tetrachloride and aluminium diethyl monochloride were mixed with a suspension of 0.5 parts of polyethylene in 15 parts by volume of iso-octane for 20 minutes at 40°

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5 C., the relative amounts of the catalyst-forming components being sufficient to give an Al/Ti ratio of 1 and a concentration of 100 millimols per litre. The polyethylene formed  
10 a support on which the catalyst was precipitated during the mixing period. Further iso-octane was then added to give a catalyst suspension in 300 parts by volume of iso-octane having a catalyst concentration of 5 millimols per litre. Aluminium chloride was then added thereto in amount to give a concentration of 5 millimols per litre of catalyst suspension. The system was maintained at 40° C. and a stream of acetylene-free ethylene passed  
15 through it for 2 hours. The resulting polymeric product was then worked-up in the usual way to decompose the catalyst and to isolate the polymer. Nineteen parts of polyethylene of intrinsic viscosity 2.4 were obtained as compared with an intrinsic viscosity of 3.5 of polyethylene produced under otherwise identical conditions in the absence of the aluminium chloride.

#### EXAMPLE II.

25 A suspension of a Zeigler catalyst in iso-

octane was prepared by adding an iso-octane solution of diethyl aluminium monochloride to an iso-octane solution of titanium tetrachloride and mixing the components at 20° C. under an atmosphere of ethylene. The quantities of the catalyst-forming components were such as to give a catalyst having an Al/Ti ratio as represented by an Al/Ti concentration of 6.5/5.0 millimols per litre of iso-octane. The catalyst suspension was then rapidly heated to the polymerisation temperature of 40° C. and ethylene containing traces of acetylene and 1% of boron trifluoride was passed through it for 2 hours. The resulting polymeric product was then worked-up to give a polymer of intrinsic viscosity 2.1 as compared with a polymer of intrinsic viscosity 2.6 obtained under otherwise identical conditions but in the absence of the boron trifluoride.

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